I. C. 7466 MAY 1948

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BY

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TRANSLATED BY O. C. RALSTON

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ELECTROLYTIC PREPARATION OF ZINC DUST[1]

By Walter Eckardt[2]

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PREFACE AND SUMMARY

By O. C. Ralston

The Bureau of Mines has under development on a technical scale an electrolytic process for treating oxidized ores of zinc, using caustic soda as an electrolyte. Whereas the Bureau process can alternately make either solid zinc or zinc dust, the following paper, from the Ludwigshafen research laboratory of the well-known I. G. Farbenindustrie, A. G., of Germany, deals only with production of zinc dust from sodium zincate solutions and may well serve as introduction to the subject for American metallurgists. The Bureau of Mines pioneered in the idea; a study on laboratory scale by H. J. Morgan and O. C. Ralston was made early in the First World War and published in Transactions of the American Electrochemical Society.[4] The Eckardt paper, translation of which follows, goes more thoroughly into the preparation of electrolytic zinc dust, and later publications of the Bureau of Mines will deal with broader details and application of the idea to treatment of low-grade ores and metallurgical intermediates, which is the point where Eckardt left off.

The Eckardt report became available through operations of Field Information Agency, Technical (FIAT) of the Office of Military Government for Germany (US), which made bibliofilm copies of the files of internal technical reports of many of the German industrial establishments. Eckardt's report is dated April 1939 and was taken on FIAT Microfilm Reel MM 106, frames 82-101, which is on file as Publication Board Document 41411 in Office of Technical Services of the U. S. Department of Commerce, Washington, D. C.

Eckardt points out that the normal source of zinc dust is the blue powder of the zinc retorts, which decreases in volume every year owing to technologic improvements in zinc smelting. I. G. saw the importance of making a

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1/ The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7466."
2/ I. G. Farbenindustrie A. G.
3/ Chief, Metallurgical Division, Bureau of Mines.
4/ Vol. 30, 1916, pp. 231-241.

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greater supply of better grade zinc powder because it is used in reducing-hydrogenation of vinylacetylene for making butadiene, an important ingredient in synthetic rubber. Moreover, it is used in preparation of hydrosulfites of zinc or sodium, which are also powerful reducing agents in the dye industry. In this latter application a solution of sulfur dioxide is reduced with zinc dust at low temperatures to form zinc hydrosulfite, which can be converted to the sodium salt by precipitating zinc carbonate. Eckardt credits the firm of Siemens & Halske, of Berlin, with development of a similar process patented in Germany in 1932.

The I. G. work pointed to use of an electrolyte containing mainly NaOh, present to the extent of 200 grams per liter and 10 grams of Zn per liter, present as sodium zincate. This is maintained at 30° C. in the electrolytic cell by using hollow iron or magnesium alloy (Elektron) cathodes cooled by circulating water through the hollow box cathode. The anode of nickel sheet is inert. Optimum current density is 120 to 150 amperes per square foot of exposed cathode surface, and at 30 mm. space between electrodes the voltage drop per cell is 3.4 volts, current efficiency 80 to 90 percent, and power consumption 3,000 kw.-hr. per metric tonne (2,720 kw.-hr. per short ton).

Conditions were chosen such that the zinc deposited on the cathodes as a loosely adherent slime that fell off by gravity or on light tapping of the cathode and collected in a V-trough bottom of the cell. The first test cell made 7 kilograms of zinc powder daily (15 pound) and the second one 50 kilograms (110 pounds). Raw material was the high grade zinc oxide of the Duisberg copper smelter or a special grade of zinc oxide. Adaptation to ores, calcines or low grade oxide recovered from primary or secondary zinc metallurgical operations was not made. Details of operation are given. Two sketches of apparatus used in the test plant are included but reveal little of construction and are omitted owing to poor reproducibility from the microfilm.

REPORT

By Walter Eckardt

The chemical industry uses large amounts of zinc dust that comes as a byproduct of zinc smelters that improve their practice and make less of it. The main uses of zinc dust are (1) in making hydrosulfites and (2) in reducing organic compounds like vinylacetylene, which is hydrogenated to butadiene (used in making synthetic rubber).

Electrolytic zinc is made in reguline form from acidic solutions, but a zinc slime will form when more noble metals than zinc are in the solution and when the electrolyte is insufficiently acid. When zinc dust is made form these solutions it can be done only at such low current densities as to be impractical.

Alkaline solutions were found more suitable, and I. G. developed a process using highly alkaline zincate solutions. Siemens & Halske are also known to have a similar process.

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Electrolysis of Zincate Solutions.

(a) The Electrolyte.

We studied the conditions for lowest energy consumption, highest yield, and best quality for the above-named two principal uses. These conditions are strongly influenced by the zinc content of the solutions. The higher the zinc content, the coarser and harder the product and the poorer the value of the product for the proposed uses. Best results were obtained in very dilute solutions, but then the current efficiency was very low. The NaOH concentration made little difference on results except that by choosing a high concentration, much higher conductance was obtained and optimum concentration is about 200 grams of NaOH per liter of electrolyte. This solution is saturated with 30 grams of zinc per liter dissolved as zinc oxide or as metal to form sodium zincate, but we found that 10 grams of zinc per liter of caustic soda of the above concentration was best-adapted to practical operation.

With rising temperature, this electrolyte increases sharply in conductance; but the rate of re-solution of the zinc sponge in it also rises, and hence yield decreases. The optimum operating temperature is 30°C., and the electrolyte must be cooled to keep down to this temperature.

Impurties like sulfate or chloride cause no trouble in electrolysis, but any dissolved iron precipitates with the zinc sponge. Any iron contaminates zinc hydrosulfite, colors it yellow, and is undesired. Hence, the iron content of the electrolyte must be kept low.

(b) Anodes.

Carbon is attacked by anodically generated oxygen and was found unsuitable for these electrolytes. Iron anodes form ferrites in solution and the sodium ferrite is to some extent reduced to metal at the cathode, the iron entering the zinc sponge and lowering its value and usefulness. Nickel anodes in the form of thin sheet were found to be unattacked and best-adapted to these solutions.

(c) Cathodes.

To make zinc dust, the zinc should be deposited as a fine slime of loose consistence and no solid underlayer should form and adhere to the cathode. The slime should either fall off spontaneously or be capable of being shaken off on light tapping of the cathode. Of all the metals tried, only iron and Elektron metal (a magnesium alloy) gave the best results. On iron there forms first a thin layer of gleaming reguline zinc, but thereafter slime zinc forms that can be shaken off. Stripping a cathode with a scraper compacts the zinc slime too much and lowers its value. Even scrapers of wire or vinyon thread caused similar troubles.

Elektron alloy formed no underlayer, and all zinc sponge fell off easily on slight tapping. This alloy has been under patent protection by Siemens & Halske since 1932.

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Cathodes were made hollow to permit the necessary water cooling mentioned above, and this solved the electrolyte cooling problem. On the corners some hard warts and knobs had to be knocked off periodically to prevent short circuits. It was determined that all parts of the cathode which do not transport much current should be "gummed" to prevent formation of solid warts.

(d) Miscellaneous.

Optimum current density at the cathode is 12-15 amp. per dm. (120-150 amp. per ft). Higher current density causes voltage drop and temperature of the cell to rise and hence calls for more cooling water - otherwise current efficiency drops. The cell voltage drop at 30°C. (13 amp. per sq. dm and 30 mm spacing, anode to cathode) is about 3.4 volts and at 70 mm spacing is 4.2 volts. Less than 30 mm spacing is difficult to maintain practically owing to danger of short circuits.

The current efficiency depends on the zinc content of the electrolyte and for the above optimum conditions it is 80 to 90 percent. With a higher zinc content, current efficiencies up to 98 percent can be had but at the price of making a zinc sponge of coarser particle size and lower activity when used for making either hydrosulfites or butadiene.

Commercial Apparatus

On the basis of the small laboratory cell tests, two larger cells were designed and operated. The first had a capacity of about 7 kilograms per day and the second, with 2,500 amperes capacity, made 50 kg. per day (110 pound). They were of the usual trough design, with rubber lined steel sides and bottom, and the bottom was a V-shaped hopper for periodical removal of sponge zinc sludge.

The low zincate solution (10 grams of zinc per liter) was made up in a steam jacketed, stirred dissolving kettle at 90°C as a saturated solution (30 grams of zinc per liter). Time to effect saturation depended on the raw material dissolved. We used a quickly dissolving zinc oxide fume and also the more slowly dissolving Duisberg zinc oxide. In any case, the solution was saturated in 8 hours. It was then cooled quietly and filter-pressed through a "Vinoflex" filter cloth into a feed tank lined with rubber on steel.

The reservoir of electrolyte was stirred and was of steel lined with rubber to keep the iron content down. It received a certain amount of new saturated solution to make up for depletion. The electrolyte of 200 grams of NaOH and 10 grams of zinc per liter was fed by gravity to the open cells, was allowed to suffer 10-percent depletion on passing through and was returned to the circulating tank by rubber-lined pump. This 10-percent depletion assured a fine-grained zinc sponge. A part of the slightly depleted solution was cut out for return to the dissolving kettle and replaced by strong zincate solution from the storage tank to keep the circulating stock constant in volume and composition.

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The steel-trough cell was rubber-lined, and the V-bottom had a large discharge valve for periodic removal of the accumulated thick sludge of zinc sponge. The reason for rubber lining of all iron parts that could contact metallic zinc sponge is the fact that iron dissolves rapidly in NaOH solutions when zinc metal is in contact with it. The cathodes hung in the upper part of the trough, and each was provided with little hammers that could be raised and dropped to jar off zinc sponge. The sponge settled into the V-hopper bottom. We used both box cathodes of iron and of Elektron, partly coated with rubber at spots where warts and knobs tended to form. The Elektron metal cathodes did not release their zinc sponge as easily in the large cell as in the laboratory cells and demanded mechanical shaking as did the iron cathodes. This may be due to hydrostatic pressure compacting the sponge. Tests are under way to study the remedy of these difficulties.

The electrolyte entered at the bottoms of the cathodes, rose and overflowed to the pump back to the reservoir. A screen held back any floating clots of slime. The zinc slime collected in the hopper bottom and was periodically flushed through the large valves to filter and wash tanks. After enough washing to leave low alkalinity the slurry was not markedly oxidized in 12 to 24 hours of storage (Translator's note: My own experience is that a slow evolution of hydrogen bubbles goes on for weeks. O.C.R.).

If filtered and dried, the slightly alkaline zinc power oxidizes rapidly in air and will even inflame spontaneously. If dried the sludge should be quickly washed with excess water and then a 1- to 2-percent ammonium sulfate solution to react with last traces of alkalinity and then be decanted. It can be washed clean on a burned clay Nutsch filter. The zinc paste has 35 to 45 percent of zinc metal and can be used in the moist condition or vacuum dried at a low temperature, but always with the sacrifice of a certain portion of the zinc being oxidized by reaction with water. Larger masses can be dried in a Vebuleth-Schaufel dryer. The metal content of the dry dust is 85 to 95 percent.

Results

The small cell was operated for 3 months, making 7 to 8 kilograms of zinc dust daily. Average current efficiency over this period was 84 percent, the energy consumption being 310 kw.-hr. per 100 kilograms of zinc (D.C.). This zinc dust effected vinal acetylene hydrogenation, with a 90-percent yield, compared to a 60-percent yield with zinc dust from the smelter. The dried powder was not used but only the 45 percent electrolytic zinc paste.

The hydrosulfite-forming efficiency of the smelter zinc dust was about 93 percent and was not equaled by the I. G. dust, which was under 90 percent at best and averaged 83 percent. Better results were had with zinc dust made on Elektron cathodes. When a paste was used instead of dried powder, the results were about equal. Hydrosulfite efficiencies varied from 91 to 95 percent. I. G. zinc dust was, in all cases, at least as reactive as smelter dust and usually more active. Deterioration of the dried dust is due to its great activity.

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Physical and Chemical Properties of Electrolytic and Smelter Zinc Dusts

Even superficially, the two types of zinc dust showed great differences, as seen in photomicrographs (not reproduced here owing to loss of detail in microfilm). The smelter dust was made up of tiny spherules of 1 to 6 microns diameter and averaging 4 microns, a form to be expected from distilled zinc. Roentgenograms (X-ray) showed each spherule to be a single crystal of hexagonal lattice.

Electrolytic zinc dust in the microscope showed a "fern-leaf" appearance, and particles looked much larger than the smelter dust, up to 45-60 microns long. X-ray examination showed each fern leaf to be a cluster of very small single crystals, each only about 0.07 micron in diameter. This structure accounts for the great reactivity of the electrolytic zinc dust.

The difference in structure also causes a great difference in bulk density of the two dusts. A liter of the smelter dust weighs 2,500 grams; 1 liter of electrolytic dust weighs 400 to 900 grams. Very light brief milling of dried electrolytic dust raises this figure to 1,900 grams. The chemical composition of the several dusts tested is:

Element, percent	Berzelius Smelter	Electrolytic dusts	
		S. & H.	I. G.
Total zinc.....	95.90	97.9	93.8
Lead.....	2.14	.23	.067
Cadmium.....	1.14	-	Trace
Iron.....	-	.061	.020
Copper.....	.0008	.005	.075
Arsenic.....	.0021	.0005	.0010

The high lead and cadmium content of the smelter dust is striking. We tested whether these two metals could enter the electrolytic dust if present in the solution. Lead entered readily and 2 percent in the resulting dust cause it to dislodge itself more readily from the cathodes, no shaking or jarring being needed. The 2 percent Pb powder gave a better hydrosulfite yield (86-90 percent) but there was no advantage in hydrogenation of vinyl acetylene. In this latter case, lead contamination is objectionable.

Cadmium will not dissolve in the caustic solutions so cannot enter electrolytic dust. Other metallic or nonmetallic additives made no better dust and in most cases are undesired.

Economics

The cost of preparation of the two zinc dusts is about equal. We are engaged in tests to displace the expensive Duisberg zinc oxide and the special zinc oxide by cheaper raw materials like zinciferous flue dusts.

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